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ABSTRACT:

PURPOSE: To reduce a trickle charge current, and heighten the effect of anticorrosion alloy of a positive electrode grid so as to attain a long life by reducing oxygen gas absorbing ability at a negative electrode in a sealed lead-acid battery used as an emergency power source and the like.

CONSTITUTION: A separator whose main component is glass fiber is interposed between a paste type positive electrode plate and a negative electrode plate. An apparent density of the separator is set to 160 to 190g/l, and the apparent density of negative electrode active material is set to 3.6 to 4.3g/cc. A positive electrode grid is of Pb-Ca-Sn alloy, and Sn content in the alloy is set to 1.4 to 2.4 percentage by weight.

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(54)【発明の名称】 密閉形鉛蓄電池

(57)【要約】

【目的】 非常用電源等に使用される密閉形鉛蓄電池に関するもので、負極での酸素ガス吸収能力を低下させることにより、トリクル充電電流を下げ、正極格子の耐食性合金の効果を高め長寿命とする。

【構成】 ペースト式の正極板と負極板の間にガラス織維を主成分としたセパレータを介在させ、セパレータはみかけ密度が160~190g/lに負極活物質はそのみかけ密度が3.6~4.3g/ccとし、正極格子をPb-Ca-Sn合金でその合金中のSnの含有量が1.4~2.4重量%とした。

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【特許請求の範囲】

【請求項1】ペースト式の正極板と負極板の間にガラス纖維を主成分としたセパレータを介在させた密閉形鉛蓄電池であって、みかけ密度が160～190g／1のセパレータとみかけ密度が3.6～4.3g／ccの負極活物質を用い、正極板の格子がPb-Ca-Sn合金からなり、この合金中のSnの含有量が1.4～2.4重量%であることを特徴とする密閉形鉛蓄電池。

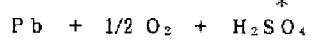
【請求項2】前記格子合金の量が正極活物質1g当たり0.6～1.0gである請求項1記載の密閉形鉛蓄電池。

【発明の詳細な説明】

【0001】

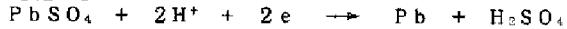
【産業上の利用分野】本発明は無停電電源装置(UPS)や非常用電源として使用される密閉形鉛蓄電池に関するものである。

【0002】



【0006】

【化3】



【0007】以上の反応からわかるように正極から発生した酸素ガスがスムーズに負極に移動できるようにセパレータは拡散性のよいものを選択しなければならない。

【0008】また密閉形鉛蓄電池はどのような姿勢、設置方向で用いても希硫酸電解液の電池外への漏れを防ぐためと、極板と電解液との電気化学的接触を保つため、希硫酸電解液は実質的に非流動化されている。このように酸素ガスの拡散と電解液を非流動化する方法として現在多くの場合、ガラス纖維を主成分とした高保液性のセパレータを極板間に配し、このセパレータ中に自由に遊離できない程度に電解液を含浸させる方法（これは通常リテナ式密閉形鉛蓄電池とよばれる）がとられている。

【0009】

【発明が解決しようとする課題】UPSや非常用電源に用いる鉛蓄電池は、停電時に瞬時に電力を供給できるよう常に定電圧充電が行われている。いわゆるトリクル充電又はフロート充電と呼ばれる充電方式をとっている。このような充電時の鉛蓄電池の寿命劣化機構は、トリクル充電により流れる充電電流により、正極格子が腐食されて電導部分の減少、あるいは腐食による格子の伸びにより正極活物質と格子との密着性が低下して、有効な活物質が減少し放電容量が低下することによる。

【0010】密閉形鉛蓄電池の場合、前述したようにトリクル充電時に、密閉化反応に伴う充電電流が流れるため、密閉化反応のない液式鉛蓄電池に比べ大きな充電電流が流れる。そのため正極格子の腐食スピードが速く、寿命が短い。

【0011】本発明はこのような課題を解決するもの

* 【従来の技術】近年電源設備用鉛蓄電池として補水、比重測定、均等充電等の保守作業が不要で、かつ設置方向を選ばない負極で酸素ガスを吸収除去する負極吸収式の密閉形鉛蓄電池の使用が増加してきた。

【0003】負極吸収式の密閉形鉛蓄電池は、充電末期状態において水の電気分解を抑えるため、負極から水素が発生する電圧より低い電圧に充電電圧を制御し、（化1）のように正極から発生した酸素ガスを速やかに負極で吸収して水に戻す（化2）の反応とともに、生成した硫酸鉛を充電により再び金属鉛に還元する反応（化3）により、電池の密閉化を可能にしている。以上の各反応を次に示す。

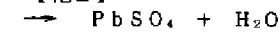
【0004】

【化1】



【0005】

【化2】



※で、トリクル充電においてその充電電流を下げ、正極格子に耐食性鉛合金を使用することにより、長寿命な密閉形鉛蓄電池を提供することを主たる目的とするものである。

【0012】

【課題を解決するための手段】本発明の密閉形鉛蓄電池は、ペースト式の正極板と負極板の間にガラス纖維を主成分としたセパレータを介在させて、みかけ密度が160～190g／1のセパレータとみかけ密度が3.6～4.3g／ccの負極活物質をそれぞれ用い、さらに正極格子がPb-Ca-Sn合金からなりこの合金中のSnの含有量を1.4～2.4重量%にしたことを特徴とする。

【0013】

【作用】密閉形鉛蓄電池のトリクル充電時の充電電流は、その密閉化能力である負極活物質の酸素吸収能力とセパレータの酸素拡散能力とに左右される。

【0014】セパレータのみかけ密度を160～190g／1にすることにより、正極から負極への酸素ガスの拡散スピードを低くする。190g／1以上では電解液の保液性が低下し、放電容量が低下する。又160g／40以下ではセパレータの孔径が大きくなり酸素ガスの拡散スピードが高まってトリクル充電時の充電電流が大きくなる。

【0015】又負極活物質のみかけ密度を3.6～4.3g／ccにすることにより、負極活物質の比表面積を下げ、酸素ガスの吸収能力を低くする。みかけ密度が4.3g／cc以上では、活物質の比表面積が小さすぎて放電能力が低下して好ましくない。又3.6g／cc以下では、活物質の比表面積が広く、酸素ガスの吸収能力が高まってトリクル充電時の充電電流が大きくなる。

【0016】トリクル充電電流を下げるためには、上記

のセパレータおよび負極活物質の両方の条件が揃えることが必要であり、どちらか一方の条件が異なるとバランスがくずれ好ましくない。

【0017】さらにトリクル充電電流を下げるだけでは、正極格子の腐食を十分に抑えることはできない。すなわち正極格子にPb-Ca-Sn合金を用い、この合金中のSn含有量を1.4~2.4重量%にすることにより、正極格子の耐食性が向上する。

【0018】ただしトリクル充電時の充電電流が大きい場合には、このSnの含有量が変化しても腐食電流が大きすぎて、耐食性に変化はみられない。充電電流の小さい場合のみ、このSn量規定の効果が見られる。

【0019】以上のように、適正なセパレータのみかけ密度及び負極活物質のみかけ密度を選ぶことにより、酸素ガス吸収反応を抑制して充電電流を下げ、さらにこの充電電流の小さな状態にて正極格子合金中のSn含有量を選定することにより、正極格子の耐食性が向上して、トリクル充電使用時の長寿命な密閉形鉛蓄電池となる。

【0020】

【実施例】以下に、本発明による実施例を説明する。

【0021】ペースト式の正、負極板とガラス纖維を主成分とするセパレータを用いて、セパレータのみかけ密度別及び負極活物質のみかけ密度別の電圧、公称容量6V100Ahの電池を作成し、トリクル充電時の充電電流を調べた。

【0022】なおセパレータの纖維径は0.6~1.0μmのものを使用した。図1はセパレータのみかけ密度別、負極活物質のみかけ密度別の6.8V定電圧充電時の充電電流を示しており、横軸は負極活物質のみかけ密度、縦軸は充電電流をそれぞれ示す。

【0023】図1よりセパレータのみかけ密度が160g/1以上でかつ負極活物質のみかけ密度が3.6g/cc以上で充電電流が最も小さくなる。しかしセパレータのみかけ密度が190g/1では、電解液の保液性が低下して放電容量は85Ahに低下した。また負極活物質のみかけ密度が4.3g/cc以上では、活物質の比表面積が小さくなりすぎ、放電容量が低下して90Ah以下であった。

【0024】またセパレータのみかけ密度が150g/1以下では、負極活物質のみかけ密度が高くなても、充電電流の大きな変化は見られない。

【0025】これらの現象は以下の内容で説明できる。すなわち、セパレータのみかけ密度が高くなると、その孔径が小さくなり、密閉化のための酸素ガスの拡散が遅くなる。また負極活物質のみかけ密度が高いと、その比表面積が小さくなり、酸素ガスとの反応面積も小さくなるため、酸素ガス吸収能力が低下する。

【0026】これらセパレータと負極活物質との相乗効果により、酸素ガスの拡散、吸収能力が低下し、酸素ガス吸収反応に伴う充電電流が低下する。

【0027】次に以上の試験電池の中から、負極活物質のみかけ密度3.9g/ccで、セパレータのみかけ密度が140g/1と170g/1の2種類（すなわち、充電電流が高いものと、低いもの）の電池を用いて、正極格子合金はPb-Ca-Sn合金とし、それぞれの合金中のSnの含有量を変化させてトリクル寿命試験を行った。

【0028】なおCaの含有量は0.09重量%の一定とした。また寿命試験は雰囲気温度を60°Cで行い、トリクル充電電圧を6.8Vの定電圧とした。3週間おきに放電容量を確認し、試験前の放電容量の70%まで容量低下した時点を寿命とした。

【0029】図2に寿命試験結果を示す。横軸は正極格子合金中のSnの含有量で、縦軸は寿命期間を示す。

【0030】図2からわかるように、充電電流の大きな電池ではSn含有量にあまり関係なく寿命は短かった。しかし充電電流の小さな電池では、Sn含有量が増えると寿命が長くなることがわかる。Snの効果は1.4~2.4重量%が最大で、2.4%以上はその効果の上昇は見られないことがわかる。また寿命になった電池を調査したところ全て充電電流による正極格子の腐食のため有効な活物質が減少して、放電容量が低下していた。なお、Snの含有量の変化による充電電流のちがいは見られなかった。

【0031】Snの効果は充電電流の小さい場合は、正極格子の耐食性を向上させることができ、含有量の増加とともに耐食効果も上がるが、実験的に2.4重量%よりも多くなっても効果の上昇はみられない。しかし充電電流が大きい場合には、Snによる耐食効果よりも充電電流による正極格子の腐食影響の方が大きくSnの効果があまり見られなかった。

【0032】さらに正極格子重量については、正極活物質1g当たり0.6~1.0gが最適であることがわかった。

【0033】すなわち耐食性が向上しても0.6g以下では、格子が細すぎてすぐに腐食劣化してしまう。

【0034】また、1.0g以上では格子体積が多くなり、正極活物質の充填できる体積が小さくなるため、取り出せる放電容量が少なくなり好ましくない。

【0035】以上のように本発明は、適正なセパレータみかけ密度、負極活物質みかけ密度、正極格子合金中のSn含有量の選定により実現できるものでありその1つが欠けても実現できない。なおこの実施例は6V100Ahの電池で実験したが、原理上からわかるように、電圧・容量に関係なく実現できる。また寿命要因が充電電流による正極格子の腐食であるため、正極活物質の密度や電解液比重には影響を受けない。

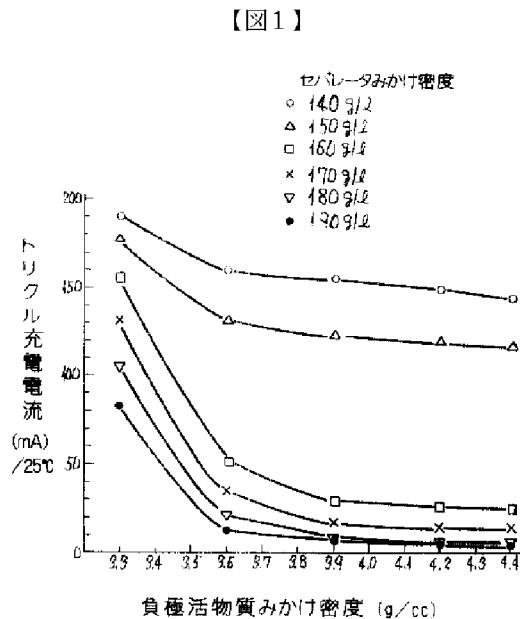
【0036】

【発明の効果】以上説明したとおり、本発明の密閉形鉛蓄電池を用いれば、トリクル充電の使用方法において長

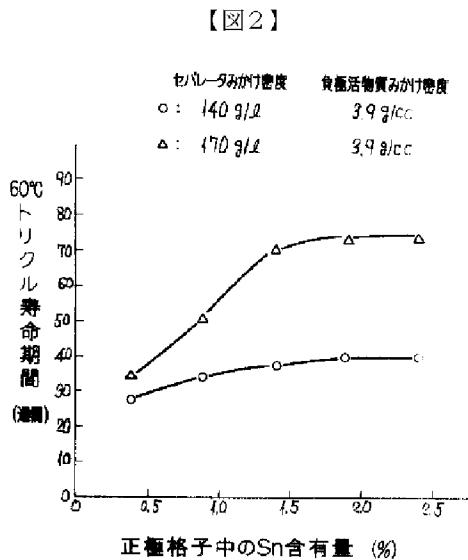
寿命の密閉形鉛蓄電池を供給することができる。

【図面の簡単な説明】

【図1】セパレータのみかけ密度別、負極活物質のみかけ密度別のトリクル充電時の充電電流の関係を示す図



【図2】充電電流が大きい場合と小さい場合の正極格子合金中のSn量別のトリクル充電時の寿命の関係を示す図



[Claim(s)]

[Claim 1] It is the sealed type lead acid battery which made the separator which made glass fiber the main ingredients intervene between paste-type a plus terminal board and a negative electrode plate. The sealed type lead acid battery characterized by the content of Sn in this alloy being 1.4 to 2.4 weight % using the separator whose appearance density is 160-190g/l, and the negative electrode active material whose appearance density is 3.6-4.3g/cc by the grid of a plus terminal board consisting of a Pb-Ca-Sn alloy.

[Claim 2] The sealed type lead acid battery according to claim 1 whose quantity of said grid alloy is per [0.6-1.0g] 1g of positive active material.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the sealed type lead acid battery used as an uninterruptible power system (UPS) or backup power.

[0002]

[Description of the Prior Art] As a lead accumulator for power supply equipment, maintenance work, such as water refilling, specific gravity measurement, and equalized charge, is unnecessary, and use of the sealed type lead acid battery of the negative electrode absorption type which carries out absorption removal of the oxygen gas with the negative electrode from which an installation direction is not chosen has increased in recent years.

[0003] In order that the sealed type lead acid battery of a negative electrode absorption type may suppress electrolysis of water in a charging end term state, [reaction / which controls charge voltage on voltage lower than the voltage which hydrogen generates from the negative electrode, absorbs promptly the oxygen gas which occurred from the plus terminal like (** 1) with the negative electrode, and is returned to water (** 2)] Sealingization of the battery is enabled by the reaction (** 3) which returns the generated lead sulfate to metal lead again by charge. Each above reaction is shown below.

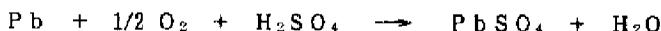
[0004]

[Chemical formula 1]



[0005]

[Chemical formula 2]



[0006]

[Chemical formula 3]



[0007] The separator must choose the good thing of diffusibility so that the oxygen gas which occurred from the plus terminal so that the above reaction might show can move to the negative electrode smoothly.

[0008] Moreover, even if it uses a sealed type lead acid battery in what kind of posture and an installation direction, in order to prevent the leakage out of the battery of a dilute

sulfuric acid electrolyte and to maintain the electrochemical contact with a plate and an electrolytic solution, immobilizing of the dilute sulfuric acid electrolyte is carried out substantially. Make diffusion and the electrolytic solution of oxygen gas into the method of carrying out immobilizing, and In thus, the case of the present many The separator of high solution retention which made glass fiber the main ingredients is allotted between plates, and the method (this is usually called a retainer type sealed type lead acid battery) of infiltrating an electrolytic solution into the grade which cannot separate freely in this separator is taken.

[0009]

[Problem to be solved by the invention] Constant-potential charge is always performed so that the lead accumulator used for UPS or backup power can supply electric power in an instant at the time of a power failure. The charge method called what is called a trickle charge or a float charge is taken. The life degradation mechanism of the lead accumulator at the time of such charge is because a positive electrode grid is corroded by the charging current which flows by a trickle charge, the adhesion of positive active material and a grid falls according to the elongation of the grid by reduction of an electrical conduction portion, or corrosion, effective active materials decrease in number and electric discharge capacity falls.

[0010] Since in the case of a sealed type lead acid battery the charging current accompanying a sealing-sized reaction flows at the time of a trickle charge as mentioned above, big charging current flows compared with a liquid type lead accumulator without a sealing-sized reaction. Therefore, the corrosion speed of a positive electrode grid is quick, and it is short-life.

[0011] It sets it as the main purpose to offer a long lasting sealed type lead acid battery by this invention's solving such a technical problem, lowering the charging current in a trickle charge, and using a corrosion-resistant lead alloy for a positive electrode grid.

[0012]

[Means for solving problem] The sealed type lead acid battery of this invention makes the separator which made glass fiber the main ingredients intervene between paste-type a plus terminal board and a negative electrode plate. A positive electrode grid is further characterized by having consisted of a Pb-Ca-Sn alloy and carrying out content of Sn in this alloy to 1.4 to 2.4weight %, using respectively the separator whose appearance density is 160-190g/l, and the negative electrode active material whose appearance density is 3.6-4.3g/cc.

[0013]

[Function] The charging current at the time of the trickle charge of a sealed type lead acid battery is influenced by the oxygen uptake capability of negative electrode active material and the oxygen diffusing capacity of a separator which are the sealing-sized capability.

[0014] By applying only a separator and density being 160-190g/l, diffusion speed of oxygen gas from a plus terminal to the negative electrode is made low. In 190g/l or more, the solution retention of an electrolytic solution falls and electric discharge capacity falls. Moreover, in 160g/l or less, the aperture of a separator becomes large, the diffusion speed of oxygen gas increases and the charging current at the time of a trickle charge becomes large.

[0015] Moreover, by covering only negative electrode active material and carrying out [cc] density in 3.6-4.3g /, the specific surface area of negative electrode active material is

lowered, and absorptance of oxygen gas is made low. Appearance density has the too small specific surface area of an active material in 4.3g/cc or more, and discharge capability falls and is not desirable. Moreover, the specific surface area of an active material is large in 3.6g/cc or less, the absorptance of oxygen gas increases and the charging current at the time of a trickle charge becomes large.

[0016] In order to lower trickle charging current, it is required for the conditions of both the above-mentioned separator and negative electrode active material to arrange, and it collapses and is not desirable [balance] if one of conditions differ.

[0017] Only by furthermore lowering trickle charging current, corrosion of a positive electrode grid cannot fully be suppressed. That is, the corrosion resistance of a positive electrode grid improves by using a Pb-Ca-Sn alloy for a positive electrode grid, and carrying out Sn content in this alloy to 1.4 to 2.4 weight %.

[0018] However, when the charging current at the time of a trickle charge is large, even if this content of Sn changes, corrosion current is too large and change is not seen by corrosion resistance. Only when charging current is small, the effect of this amount regulation of Sn(s) is seen.

[0019] As mentioned above, by applying only a proper separator, covering only density and negative electrode active material, and choosing density By inhibiting an oxygen gas absorption reaction, lowering charging current, and selecting Sn content in a positive electrode grid alloy in the state where this charging current is still smaller, the corrosion resistance of a positive electrode grid improves and it becomes a long lasting sealed type lead acid battery at the time of trickle charge use.

[0020]

[Working example] Below, the work example by this invention is explained.

[0021] Using the separator which makes the main ingredients positive, the negative electrode plate, and glass fiber of a paste type, only the separator was applied, only a density exception and negative electrode active material were covered, the voltage according to density and the battery of nominal capacity 6V100Ah were created, and the charging current at the time of a trickle charge was investigated.

[0022] In addition, the diameter of a fiber of the separator used the 0.6-1.0-micrometer thing. Drawing 1 applies only a separator, in a density exception, only negative electrode active material is covered, the charging current at the time of the 6.8V constant-potential charge according to density is shown, a horizontal axis covers only negative electrode active material, and density and a vertical axis show charging current, respectively.

[0023] Only a separator is applied from drawing 1, density is 160g/l or more, and only negative electrode active material is covered, and, in charging current, density becomes the smallest 3.6g/cc or more. However, only the separator was applied, in 190g/l, the solution retention of the electrolytic solution fell and, as for electric discharge capacity, density fell to 85Ah. Moreover, only negative electrode active material was covered, in density, the specific surface area of the active material became small too much in 4.3g/cc or more, electric discharge capacity fell, and they were 90 or less Ah.

[0024] Moreover, even if it applies only a separator, density covers only negative electrode active material in 150g/l or less and density becomes high, a big change of charging current is not seen.

[0025] The following contents can explain these phenomena. That is, if only a separator is applied and density becomes high, the aperture will become small and diffusion of

oxygen gas for sealing-izing will become slow. Moreover, since the specific surface area will become small and will become small [reaction area with oxygen gas] if only negative electrode active material is covered and density is high, oxygen gas absorptance declines.

[0026] According to the synergistic effect of these separators and negative electrode active material, diffusion of oxygen gas and absorptance decline and the charging current accompanying an oxygen gas absorption reaction falls.

[0027] Next, out of the above testing cell, only negative electrode active material covers it and [the density of 3.9g/cc] Only the separator was applied, and using two kinds (namely, what has high charging current and a low thing) of batteries, 140g/l and 170g/l, density used the positive electrode grid alloy as the Pb-Ca-Sn alloy, changed the content of Sn in each alloy, and did trickle life test.

[0028] In addition, content of Ca was taken as 0.09weight % of regularity. Moreover, life test performed ambient temperature at 60 degrees C, and made trickle charge voltage the constant voltage of 6.8V. Electric discharge capacity was checked every three weeks, and the time of carrying out capacity lowering to 70% of the electric discharge capacity before an examination was made into the life.

[0029] A life test result is shown in drawing 2. A horizontal axis is the content of Sn in a positive electrode grid alloy, and a vertical axis shows a life period.

[0030] Not much regardless of Sn content with the big battery of charging current, it was short-life so that drawing 2 might show. However, by the small battery of charging current, when Sn content increases, it turns out that a life becomes long. 1.4 to 2.4 weight % of the effect of Sn is the maximum, and it turns out that the rise of the effect is not seen 2.4% or more. Moreover, when the battery which became a life was investigated, effective active materials decreased in number altogether for the corrosion of the positive electrode grid by charging current, and electric discharge capacity was falling. In addition, the difference in the charging current by change of the content of Sn was not seen.

[0031] When the charging current of the effect of Sn is small, the corrosion resistance of a positive electrode grid can be raised, and the anti-corrosion effect also goes up with the increase in content, but the rise of an effect is not seen even if it increases more than 2.4 weight % experimentally. However, when charging current was large, the corrosion influence of the positive electrode grid by charging current is greater than the anti-corrosion effect by Sn, and the effect of Sn was seldom seen.

[0032] Furthermore about positive electrode grid weight, it turned out that per [0.6-1.0g] 1g of positive active material are the optimal.

[0033] That is, even if corrosion resistance improves, in 0.6g or less, a grid will be too thin and will carry out corrosive deterioration immediately.

[0034] Moreover, since the volume which a lattice body product increases and can fill up cathode active material volume with 1.0g or more becomes small, the electric discharge capacity which can be taken out decreases and it is not desirable.

[0035] As mentioned above, this invention is unrealizable, even if selection of Sn content in proper separator appearance density, negative-electrode-active-material appearance density, and a positive electrode grid alloy can realize and one of them is missing. In addition, although experimented by the battery of 6V100Ah, this work example is realizable regardless of voltage and capacity so that it may understand from a principle.

Moreover, since a life factor is the corrosion of the positive electrode grid by charging current, influence is not received in the density or the electrolytic solution specific gravity of positive active material.

[0036]

[Effect of the Invention] If the sealed type lead acid battery of this invention is used as explained above, in the directions for use of a trickle charge, a long lasting sealed type lead acid battery can be supplied.